REMARKS

Claims 1-19 are presently pending in the application.

Claim 10-14 were amended for formalistic reasons as requested by the Examiner to more clearly recite which aspect of claim 1 is being further specified in claims 10-14. Claim 14 was also amended to recite that A can be 2% to 10%, rather than 2% or 10%, since A is part of a polygon defined by the points a) – d) of claim 1. New claim 19 has been added, and recites the first embodiment of claim 1. No new matter has been added, and Applicants respectfully request that the above amendments to the claims be entered.

The Examiner has objected to claims 10-14 for formalistic reasons. Specifically, the Examiner believes that claims 10-14 need to be drafted to clarify which aspect of claim 1 (from which claims 10-14 depend) is being further specified. Applicants believe that claims 10-14 are appropriately drafted, since the recitation of a range for Zr, Co, or A readily identifies which aspect of claim 1 is being further specified. However, Applicants have amended claims 10-14 to expressly identify the aspect of claim 1 which is being further specified to address the Examiner's requirement for correction. Accordingly, Applicants respectfully request that the objection to claims 10-14 be withdrawn.

Claims 1-18 have been rejected under 35 U.S.C. §103(a) as being unpatentable (obvious) over US 2003/0090202 (Gallitognotta). Regarding claim 1, the Examiner alleges that Gallitognotta discloses a cathode (11) comprising a metallic bearing part (12) at least partially coated with a layer of getter material (21), wherein the getter material is made of alloys consisting of vanadium and yttrium (paragraph 16). The Examiner acknowledges that Gallitognotta does not disclose that the alloys have yttrium of at least 70% by weight, but concludes that it would have been obvious to optimize the amount of yttrium to be at least 70%. The Examiner also contends that the features of claims 2-18 are either disclosed or obvious in view of Gallitognotta. Applicants respectfully but strenuously traverse the rejection of claims 1-18 for the reasons set forth below.

Claim 1 recites, *inter alia*, an alloy consisting of yttrium and vanadium. The Examiner cites to paragraph 16 of Gallitognotta for this proposition. Applicants respectfully disagree with this interpretation of Gallitognotta. At paragraph [0016], Gallitognotta discloses:

> "The getter layer can be made of any <u>one</u> of the metals that are known to have a high reactivity with gases, which <u>metals</u> essentially are titanium, vanadium yttrium, zirconium, niobium, hafnium and tantalum." (emphasis added).

The reference to "vanadium yttrium" is clearly a reference to vanadium or yttrium, and should have included a comma between the two metals. The missing comma is the result of a typographical error. The disclosure of a "metal" (as opposed to an alloy) and the structure of the sentence make clear that the getter layer is not an alloy, and is a single metal.

Moreover, at paragraph [0016], Gallitognotta subsequently discloses: "In an <u>alternative</u> embodiment, it is possible to use a getter <u>alloy</u>." Thus, if an alternative embodiment discloses alloys, this further supports the proposition that the recitation of "vanadium yttrium" (i.e., not the alternative embodiment) is that of vanadium <u>or</u> yttrium since it is the alternative embodiment which is directed to alloys. Thus, Gallitognotta fails to disclose or suggest an alloy consisting of yttrium and vanadium.

Additionally, there is no disclosure in Gallitognotta of an yttrium and vanadium alloy containing at least 70% by weight of yttrium. Although the Examiner concludes that it would have been obvious to optimize 70% by weight of yttrium and states that mere range limitations are obvious, Applicants respectfully disagree. There is absolutely no teaching in Gallitognotta that the amount of yttrium in an alloy is a factor for consideration. The courts have made clear that the discovery of an optimum value of a variable is <u>not obvious</u> if the parameter optimized is not recognized to be a result-effective variable. *See In re Antonie*, 195 USPQ 6, 8-9 (CCPA 1977) (emphasis added). The Examiner has not demonstrated that Gallitognotta discloses that in an alloy of yttrium and vanadium, the amount of yttrium is a result-effective variable.

Moreover, although the Examiner concludes that it would have been obvious to "optimize" an alloy of yttrium and vanadium such that the amount of yttrium would be more

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than 70%, the Examiner has not provided any reason for such optimization. For example, the Examiner has not identified what advantages recognized in Gallitognotta would be optimized when yttrium is more than 70% rather than less. The Examiner is inappropriately utilizing hindsight reasoning to arrive at the claimed invention without support in the cited art. Thus, claim 1 is distinguishable over Gallitognotta for this reason as well.

Additionally, the present invention utilizes alloys which are not specifically known for use in cold cathode lamps, especially to reduce the work function value of the lamps. Thus, the present invention is unobvious over the prior art. In fact, while a number of materials are known, for use as getters, the inventors of the present invention have discovered getter materials which surprisingly, will simultaneously lower the work function value of a cold cathode lamp. This further demonstrates the unobviousness of the present invention.

The disclosure at paragraph [0018] of Gallitognotta, as relied upon by the Examiner to show that the present invention is expected, is inapposite here. Paragraph [0018] of Gallitognotta merely discloses:

> "The layer of getter material does not alter the functionality of the cathode, as it was observed that these materials have work function values not exceeding those of the metals employed to produce cylindrical hollow part 12, and consequently the electronic emissive power of the cathode is not reduced."

There is no disclosure or suggestion at paragraph [0018] of Gallitognotta of optimizing the reduction of work function of a lamp. As long as the materials do not alter the functionality of the cathode, this is sufficient for Gallitognotta. There is no hint of materials which simultaneously excel as getter materials and for reducing the work function value of a lamp.

Furthermore, known art in the area of solid state physics regarding work functions has mainly comprised data relating to single elements, making the work function value of alloys generally unpredictable with such data. For example, attached as Appendix A is an extract from the *American Institute of Physics Handbook*, Third Edition, pages 9-172 to 9-186 (1972), which lists values of the work function for single elements and for very few compounds, and does not

mention values for alloys. This supports the proposition that the claimed invention is unique in its use of alloys for the reduction of work function, since it is individual materials and compounds whose work functions have normally been determined.

While the poster *Electronic Work Function of Melts of Na-K-Cs and Na-K-Rb*, which was presented on June 25, 2003 at the Fifteenth Symposium on Thermophysical Properties, in Boulder, Colorado (see Appendix B), does disclose the work function of some alloys, those alloys are different from the claimed invention. Moreover, the article at Appendix B shows that the alloys have an unpredictable work function value, often depending on the composition of the alloy in a non-linear way. For example, please see, in Fig. 2 of Appendix B, the non-linear trend of curves 2-7. This unpredictability would discourage one of ordinary skill in the art to try to make alloys of different components to reduce work functions and would discourage the "optimization" of combinations of components, since there would not be a linear way to reach a desired objective. Thus, there would not be an expectation of success in attempting to find a way to "optimize" the types and amounts of components in alloys to reduce work function. Moreover, Gallitognotta does not disclose or suggest using alloys to reduce the work function value of a cold cathode lamp, as stated above.

Also, for some alloys with additional components, the situation is even more unpredictable. For example, regarding the ZrCoA alloy of the claimed invention, according to Appendix A, the work function for Zr is between 3.6 and 4.33, for Co it is between 4.12 and 4.25, and for La (A can be La in claim 1), it is about 3. Surprisingly, however, the alloys of the claimed invention have work functions close to those of the lowest abundant element A. Thus, although the concentration of A, as claimed, is only 2 to 10%, resulting alloys have work functions close to that of A, as is clear from, for example, Example 1 of the specification. In Example 1, the vast majority of the alloy is Zr and Co, but the resulting work function is about 3 eV, in contrast to the 3.6-4.33 for Zr itself and 4.12-4.25 for Co itself. Thus, advantageous results of the present invention are surprising and result in alloys with work functions close to components which are only small fractions of such alloys.

Furthermore, during the operation of the cold cathode lamp, the getter material sorbs the undesired species. Pursuant to the *Handbook of Physics,* E.U. Condon, PhD. et al, Chapter 6, pp. 8-74 to 8-82, McGraw Hill Book Company, Inc. (1958) (see Appendix C) at pages 8-80 to 8-82, sorption can have an unpredictable effects on the work function of an alloy. However, the claimed invention surprisingly maintains a low work function of the cathode even after gas sorption.

In view of the above, there is no teaching in the cited art to arrive at the recited compositions and the recited ranges. Also, the present invention exhibits advantageously surprising results. Accordingly, it is the Applicants' position that the claimed invention is not obvious over the cited art.

Additionally, regarding claims 10-14, the Examiner states at page 5 of the Office Action that Gallitognotta does not specifically disclose the getter material comprising an alloy having zirconium, cobalt, and at least one component selected from yttrium, lanthanum, and rare earths having the component ranges recited in claims 10-14, but he concludes that it would have been obvious to obtain such alloys through "routine experimentation and optimization."

However, the Examiner has not identified where in Gallitognotta is a disclosure of alloys including zirconium, cobalt, and at least one component selected from yttrium, lanthanum, and rare earths. As explained above, the Examiner's reliance on paragraph [0018] of Gallitognotta is misplaced since the listing of metals is for individual use, not for use as alloys. Moreover, the Examiner has not identified where the use of cobalt is disclosed. Thus, the Examiner has not identified in Gallotignotta the teaching of the recited alloy components and therefore has not demonstrated *prima facie* obviousness.

While the Examiner "notes" that Amiotti discloses a getter material having 80.8% Zr, 14.2% Co, and 5% yttrium, Applicants note that Amiotti is not directed to a cathode and that there is no disclosed or suggested reason for one or ordinary skill in the art to use the getter material of Amiotti on a cathode. Also, there is no reason for one of ordinary skill in the art to change the ratios of the components disclosed in Amiotti to arrive at the claimed invention. Thus, the disclosure in Amiotti is not indicative of obviousness. In fact, the Examiner has

removed Amiotti as a reference, and it is Applicants' position that Amiotti is not an appropriate reference to reject the present claims at least because it is not directed to cathodes, as is the claimed invention, and also because it is directed to a composition with different ratios of elements.

Furthermore, the Examiner has not identified a reason taught or suggested in Gallitognotta to optimize the three recited components in the first place. There is nothing in Gallitognotta that discloses or suggests that the ratio of zirconium, cobalt, and at least one component selected from yttrium, lanthanum, and rare earths is something that would have been of interest to one of ordinary skill in the art. The necessary expectation of success for the alleged optimization is not present since there is no particular goal that has been identified regarding the mixture of the three components in an alloy. Additionally, the Examiner has not identified why the "optimization" would result in the recited ranges, as opposed to any of the myriad of other ranges possible. Although the Examiner says that motivation for removing contaminant material effectively is present, the Examiner has not demonstrated why one of ordinary skill in the art would have arrived at the recited ranges in order to optimize the removal of contaminant material. Thus, *prima facie* obviousness has not been demonstrated. Accordingly, claims 10-14 (as well as new claim 19) are patentable for this reason in addition to the above.
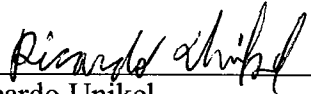
In view of the above, Reconsideration and withdrawal of the rejection of claims 1-18 are respectfully solicited, and notice of the patentability of claim 19 is also respectfully requested.

CONCLUSION

In view of the foregoing Remarks, Applicants respectfully submit that the claims are in proper form and distinguish over the cited art. Therefore, the present application is in condition for allowance. Reconsideration and an early Notice of Allowance are respectfully requested.

Dated: Dec 18, 2009

Respectfully submitted,

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Enc.: Appendices A, B, and C.

Appendix A

American Institute
of Physics Handbook
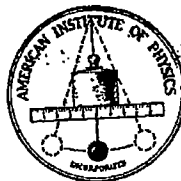
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9j. Work Function and Secondary Emission

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9j-1. Work Function Measurements. The work function ϕ of a substance is given as the difference in energy between the Fermi level (or electrochemical potential) of a solid and the electrostatic surface potential just outside. This is what is generally measured in thermionic (Th) and contact potential (C.P.D.) measurements. The photoelectric "work function" (P.E.), however, is normally taken as the measure of the photoelectric threshold and represents the energy difference between the level of the highest-lying electron at room temperature and the electrostatic surface potential. Although the highest-energy electron of a metal at room temperature is very near the Fermi level, this is not necessarily true for semiconductors. (This fact must be kept in mind when one is comparing photoelectric work functions of semiconductors with those derived from thermionic or contact potential techniques.) Table 9j-1 lists the work functions of elements as determined by *thermionic, photoelectric,* and *contact potential* difference methods, while Table 9j-2 gives the thermionic work functions of various compounds used in electron emitter applications.

The thermionic work function ϕ as a rule is obtained by analyzing the emitted current by means of the Richardson equation:

$$J = 120T^2 e^{-\phi/kT}$$

where J in the current density in amp/cm², T is the absolute temperature, k is $8.62 \cdot 10^{-5}$ eV/deg, and ϕ is given in electron volts. ϕ is usually not constant in the temperature range of measurement but for most substances can be expressed in terms of a linear temperature dependence $\phi = \phi_0 + \alpha T$, where ϕ_0 is the temperature-independent component of the work function, and α is the temperature coefficient.

In many thermionic measurements, unfortunately, the work function quoted and subsequently recorded in review articles is the value obtained from the slope of a Richardson plot (log J/T^2 vs. $1/T$, which is just ϕ_0. If there is an appreciable temperature dependence, this value can be highly erroneous since these measurements are obtained at fairly high temperatures (i.e., 1000 to 2000 K). Consequently, unless the temperature dependence can be determined from the published data by some other method (e.g., from the intercept of the Richardson plot or "Richardson A value") the results are not included in this review. Furthermore, since the linear approximation to the temperature dependence very likely does not hold for all temperatures, the temperature range in which the measurements were made is also included.

Except where specifically noted, the photoelectric work function measurements are carried out at room temperature and therefore require no additional information regarding temperature range. The same is also true of contact potential difference measurements which are normally obtained at room temperature by measuring the difference in electrostatic surface potential between a substance having a known work function value or "standard" (e.g., W, Hg, Ag, etc.), and the substance to be measured.

TABLE 9j-1. Work Functions of the Elements

Element	Work function eV	Technique	Notes	Reference	Year
Ag...........	$4.31 + 0.1 \times 10^{-4}T$ 1160-1200 K	Th	1	1	1953
	4.32 1230 K	Th	2	2	1956
	4.5	P.E.	....	3	1950
	4.3	P.E.	....	4	1953
	4.32	C.P.D.	8, 4	5	1951
	4.3	C.P.D.	4, 5	6	1964
	4.44	C.P.D.	4, 6	6	1964
	4.29	C.P.D.	4, 7	6	1964
Al...........	4.36	P.E.	....	7	1936
	4.08	P.E.	....	8	1936
	4.2	P.E.	....	9	1944
	4.24	C.P.D.	8, 4	5	1951
	4.19	C.P.D.	4, 5	10	1957
	4.18	C.P.D.	5, 8	11	1966
Au...........	$4.25 + 0.15 \times 10^{-4}T$ 1160-1280 K	Th	9	1	1953
	5.1	P.E.	9	12	1961
	5.4	P.E.	9	13	1966
	5.45	C.P.D.	9, 10	14	1966
	5.22	C.P.D.	5, 9, 11	15	1966
	5.4	C.P.D.	5, 9, 10	13	1966
As...........	4.66	P.E.	....	16	1949
	4.72	P.E.	....	17	1949
Ba...........	$2.3 + 5 \times 10^{-4}T$ 1000-1300 K	Th	2	18	1965
	2.49	P.E.	....	19	1939
	2.48	P.E.	....	20	1940
	2.42	C.P.D.	3	21	1935
	2.35	C.P.D.	5	22	1941
	2.66	C.P.D.	6	23	1952
	2.5	C.P.D.	....	24	1968
B............	4.4-4.6	P.E.	....	25	1948
Be...........	3.67 920-1180 K	Th	....	26	1966
	3.3	P.E.	....	27	1934
	3.92	P.E.	....	28	1937
	3.89	C.P.D.	12	29	1968
Bi...........	4.31	P.E.	....	30	1936
	4.46	P.E.	....	31	1941
	4.34	P.E.	....	17	1949
C............	$4.39 + 1.7 \times 10^{-4}T$ 1300-2200 K	Th	....	32	1947
	$4.6 + 0.6 \times 10^{-4}T$ 1490-1670 K	Th	1	33	1952
	4.81	P.E.	....	34	1926
Ca...........	3.2	P.E.	....	35	1932
	2.7	P.E	....	36	1936
	3.21	P.E	....	37	1937
Cd...........	4.07	P.E.	....	38	1931
	4.099	P.E.	....	9	1944
	4.0	C.P.D.	13	39	1953
	4.22	C.P.D.	4, 6	40	1955
Ce...........	$2.48 + 1.8 \times 10^{-4}T$ 1060-1450 K	Th	2, 4	41	1926
	2.84	P.E.	....	35	1932

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TABLE 9j-1. WORK FUNCTIONS OF THE ELEMENTS (Continued)

Element	Work function eV	Technique	Notes	Reference	Year
Co..........	$4.4 + 0.9 \times 10^{-4}T$ ≃1200–1450 K	Th	....	42	1942
	$4.41 + 0.6 \times 10^{-4}T$ 1410–1590 K	Th	1	43	1952
	4.12	P.E.	14	44	1931
	4.25	P.E.	15	44	1931
Cr...........	$4.58 + 0.6 \times 10^{-4}T$ 1450–1600 K	Th	1	43	1952
	≃3.9 1100–1400 K	Th	....	26	1966
	4.4	P.E.	....	12	1961
Cs..........	≃1.86 ~500 K	Th	....	45	1966
	2.14	P.E.	....	46	1964
	1.84	C.P.D.	3, 4	6	1964
Cu..........	4.5 1160–1280 K	Th	1	1	1953
	4.6 ~1350 K	Th	....	2	1956
	4.4 1100–1300 K	Th	....	26	1966
	4.76	P.E.	....	47	1934
	4.86(111)	P.E.	....	48	1935
	5.61(110)	P.E.	....	48	1935
	4.60	C.P.D.	3, 4	5	1951
	4.51	C.P.D.	4, 5	10	1957
Er...........	$2.97 + 0.65 \times 10^{-4}T$ 1150–1500 K	Th	....	48a	1967
Fe...........	$\phi_\beta = 4.48 + 1.3 \times 10^{-4}T$	Th	....	42	1942
	$\phi_\gamma = 4.21 + 3.75 \times 10^{-4}T$ ≃1200–1450 K	Th	....	42	1942
	$4.31 + 0.6 \times 10^{-4}$ 1410–1610 K	Th	1	43	1952
	4.5 1200–1500 K	Th	....	26	1966
	$\phi_\beta = 4.62$	P.E.	....	49	1953
	$\phi_\gamma = 4.68$	P.E.	....	49	1953
	4.16	C.P.D.	4, 5	10	1957
	3.8	C.P.D.	16	50	1938
Ga..........	≃3.5 ~900 K	Th	....	2	1956
Ge..........	4.11(111)	P.E.	....	51	1959
Hf...........	$3.6 + 1.4 \times 10^{-4}T$ 1250–1820 K	Th	....	52	1957
	3.85 ~1000–1700 K	Th	2	53	1962
Hg..........	4.52	P.E.	....	54	1931
	4.5	P.E.	....	55	1934
Ir...........	$5.3 + 0.2 \times 10^{-4}T$ 1700–2200 K	Th	....	56	1951
	$5.4 - 0.3 \times 10^{-4}T$ 1590–2320 K	Th	....	57	1956
	≃5.28 1300–2000 K	Th	....	58	1966
	4.57	C.P.D.	16	50	1938
K............	2.24	P.E.	....	59	1932
	2.26	P.E.	....	60	1937

Element	
La............	≃3 / 1
Li............	2.4 / 1.4
Mg..........	3.6 / 3.1
Mn..........	3.8 / 1 / 3.7
Mo..........	4.2 / 1 / 4.8 / 4.5 / 4.
Na..........	2. / 2. / 2.
Nb..........	4. / 4.
Nd..........	≃ / 4 / 4 / 4 / 4 / ≃
Ni............	5 / 4 / 4 / 6 / ...
Os............	
Pb..........	
Pd..........	
Pr............	

TABLE 9j-1. WORK FUNCTIONS OF THE ELEMENTS (Continued)

Element	Work function eV	Technique	Notes	Reference	Year
La..........	≃3.0 1200–1500 K	Th	2	41	1926
Li...........	2.42	P.E.	....	47	1934
	1.4	C.P.D.	16	50	1938
Mg..........	3.66	P.E.	....	61	1964
	3.12	C.P.D.	13	62	1951
Mn..........	$3.83 + 1.1 \times 10^{-4} T$ 1370–1520 K	Th	1	43	1952
	3.76	P.E.	....	47	1934
Mo..........	$4.38 - 0.25 \times 10^{-4} T$ 1410–2110 K	Th	....	52	1957
	$4.33 + 0.1 \times 10^{-4} T$ ~1800–1900 K	Th	....	63	1962
	4.25 1600 K	Th	....	64	1966
	$4.33 - 1.52 \times 10^{-4} T$ 1200–2000 K	Th	....	58	1966
	4.41	P.E.	....	63	1962
	4.20	C.P.D.	4	6	1964
Na..........	2.06	P.E.	....	47	1934
	2.29	P.E.	....	28	1937
	2.28	P.E.	....	20	1940
Nb..........	4.0 1400–2100 K	Th	....	65	1964
	4.8 2200 K	Th	....	66	1964
	≃4.19 1050–2100 K	Th	....	58	1966
	4.38(110)	P.E.	....	67	1963
	4.55(335)	P.E.	....	67	1963
	4.66(111)	P.E.	....	67	1963
	4.38	C.P.D.	4	68	1964
Nd..........	≃2.95 1150–1450 K	Th	2	41	1926
Ni...........	$5.24 + 0.75 \times 10^{-4} T$ ≃1100 K	Th	....	69	1949
	4.5 1410–1610 K	Th	1	43	1952
	4.41 1170–1250 K	Th	....	26	1966
	$5.27 - 1.0 \times 10^{-3} T$ 1380–1500 K	Th	....	28	1966
	5.05 T = 628 K	P.E.	....	69	1949
	5.2 T = 1108 K	P.E.	....	69	1949
	4.78	C.P.D.	4, 5	10	1957
	5.22	C.P.D.	10	14	1966
Os...........	$5.43 - 3.9 \times 10^{-4} T$ 1413–1640 K	Th	....	58	1966
	≃5.17 ~1500 K(?)	Th	....	70	1967
	5.93	P.E.	....	71	1966
Pb..........	3.97	P.E.	....	72	1928
	3.49	C.P.D.	13	62	1951
	3.83	C.P.D.	4, 5	73	1956
Pd..........	4.64	C.P.D.	13	39	1958
Pr...........	$2.57 + 1.5 \times 10^{-4} T$ 1120–1410 K	Th	2	41	1926

TABLE 9j-1. WORK FUNCTIONS OF THE ELEMENTS (Continued)

Element	Work function eV	Technique	Notes	Reference	Year
Pt..........	5.3–5.5 ~1600–1900 K(?)	Th	....	74	1950
	5.03 + 4.2 × $10^{-4}T$ 1620–1946 K	Th	....	26	1966
	4.82	C.P.D.	13	39	1953
Rb..........	2.09	P.E.	....	59	1932
Re..........	4.85 + 0.6 × $10^{-4}T$ 1470–2150 K	Th	....	75	1963
	4.7 + 0.75 × $10^{-4}T$ 1820–2860 K	Th	....	76	1963
	4.8 1600–2200 K	Th	....	65	1964
	4.96 1325–2250 K	Th	....	58	1966
Rh..........	4.8 + 1.1 × $10^{-4}T$ ~1500–1900 K(?)	Th	....	77	1938
	4.9 + 0.2 × $10^{-4}T$ 1550–1950 K	Th	....	56	1951
	4.92	P.E.	....	78	1931
Ru..........	4.52	C.P.D.	16	50	1938
Sb..........	4.01	P.E.	....	79	1937
	4.6	P.E.	....	17	1949
	4.14	C.P.D.	16	50	1938
	4.1	C.P.D.	3, 4	6	1964
Sc..........	3.18 + 0.8 × $10^{-4}T$ 1150–1500 K	Th	....	48a	1967
Se..........	5.11	P.E.	....	47	1934
Si..........	4.42	C.P.D.	16	50	1938
	3.59 + 2.3 × $10^{-4}T$ 1250–1700 K	Th	....	32	1947
	4.02 + 2.6 × $10^{-4}T$ 1373–1623 K	Th	....	80	1953
	5.4 (111)	P.E.	....	81	1962
	3.95 (n type)	C.P.D.	17	82	1947
	4.2 (p type)	C.P.D.	17	82	1947
	4.5 (n or p)	C.P.D.	18	83	1949
Sm..........	~3.15 1150–1600 K	Th	2	41	1926
Sn..........	3.62	P.E.	....	72	1928
	4.21 liquid	P.E.	....	84	1929
	4.38 α phase	P.E.	....	84	1929
	4.50 β phase	P.E.	....	84	1929
	4.21	C.P.D.	13	85	1952
	4.42	C.P.D.	19	86	1963
Sr..........	2.3 + 0.5 × $10^{-4}T$ 850–950 K	Th	20	87	1955
	2.24	P.E.	....	47	1934
	2.74	P.E.	....	88	1938
Ta..........	4.35 300–1860 K	Th	21	89	1957
	4.25 1100–2200 K	Th	....	58	1966
	4.33 + 0.25 × $10^{-4}T$ 1700–2230 K	Th	....	90	1966
	4.1	P.E.	....	35	1932
	4.05	P.E.	....	91	1935
	4.22	C.P.D.	4	6	1964

TABL

Element

Te..........
Th..........

Ti.......

Tl..........
U..........

V..........

W..........

Y..........
Zn..........

TABLE 9j-1. WORK FUNCTIONS OF THE ELEMENTS (Continued)

Left (continued) column:

Main table:

Element	Work function eV	Technique	Notes	Reference	Year
Te...........	5.0	P.E.	....	92	1953
	4.7	O.P.D.	16	50	1938
Th...........	$3.38 + 0.45 \times 10^{-4}T$ 1250–1800 K	Th	....	93	1926
	$\simeq 3.4$	P.E.	....	85	1932
	3.66	P.E.	....	47	1934
	3.46	O.P.D.	16	50	1938
	3.71	C.P.D.	7	94	1962
	3.44	C.P.D.	3	94	1962
Tl........	$3.95 + 0.85 \times 10^{-4}T$ 1370–1520 K	Th	1	48	1952
	4.0 1300–1600 K	Th	....	65	1964
	4.45	P.E.	....	95	1954
	4.14	O.P.D.	16	50	1938
Tl...........	3.68	P.E.	....	96	1935
	3.84	C.P.D.	16	50	1938
U...........	$3.0 + 2.7 \times 10^{-4}T$ 1250–1400 K	Th	20	96	1959
	3.47 1250–1400 K	Th	22	96	1959
	$2.9 + 2.3 \times 10^{-4}T$ 1020–2000 K	Th	20	76	1963
	$\simeq 3.55$ 1000–1500 K	Th	22	97	1967
	3.47 (α)	P.E.	....	98	1962
	3.52 (β)	P.E.	....	98	1962
	3.39 (γ)	P.E.	....	98	1962
	3.65 (α)	P.E.	....	99	1967
	3.59 (β)	P.E.	....	99	1967
	3.45 (γ)	P.E.	....	99	1967
	3.19	C.P.D.	3, 4	100	1962
	3.63 (α)	C.P.D.	4	97	1967
	3.58 (β)	C.P.D.	4	97	1967
	3.53 (γ)	C.P.D.	4	97	1967
V...........	$4.12 + 0.75 \times 10^{-4}T$ 1410–1540 K	Th	1	43	1952
	3.77	P.E.	....	47	1934
	4.44	O.P.D.	16	50	1938
W...........	$4.52 + 0.6 \times 10^{-4}T$ 1350–2200 K	Th	....	101	1950
	$4.5 + 0.15 \times 10^{-4}T$ 1820–2940 K	Th	....	76	1963
	$4.58 + 0.15 \times 10^{-4}T$ 2100–2600 K	Th	....	90	1966
	4.52 1150–2200 K	Th	....	58	1966
	4.6	P.E.	....	35	1932
	4.565	P.E.	....	102	1935
	4.49	P.E.	....	103	1948
	4.55	C.P.D.	4, 5	10	1957
Y...........	$2.95 + 0.2 \times 10^{-4}T$ 1150–1400 K	Th	....	48a	1967
Zn...........	4.26	P.E.	....	104	1940
	4.307	P.E.	....	9	1944
	4.11	C.P.D.	4	105	1940
	4.22	C.P.D.	13	85	1952

TABLE 9j-1. WORK FUNCTIONS OF THE ELEMENTS (*Continued*)

Element	Work function eV	Technique	Notes	Reference	Year
Zr............	3.78	Th	....	106	1951
	$T = ?$				
	3.73 ...	P.E.	....	35	1932
	4.33	P.E.	....	95	1954
	3.60	C.P.D.	16	50	1938

However, since the resulting work function values depend on the accuracy with which the work function of the standard is known, the substance used for the standard and its assumed work function are also included:

Some of the earlier work function measurements quoted in other reference works are omitted here, especially where an appreciable number of results on the same subject have been recently published employing more refined experimental techniques. That is not to say, however, that "recentness" is synonomous with "cleanliness"; rather, the most recent studies involving techniques such as low-energy electron diffraction and Auger spectrum analysis serve to show how contaminated "clean" surfaces really are. Consequently, the values listed here merely serve to indicate the measured values of the work functions as they are presently limited by experimental refinement of measuring methods. For some substances which can be easily cleaned they are quite accurate; for others they will most certainly be considered outdated by the next review.

Notes for Table 9j-1

1. Effusion method.
2. Deduced from published results.
3. Film on W substrate.
4. Assuming ϕ for bulk W is 4.54.
5. Film on glass substrate.
6. Film on Ta substrate.
7. Bulk.
8. Assuming ϕ of Au is 5.22.
9. No Hg contamination.
10. Absolute work function value using field-emission-retarding potential method.
11. Assuming ϕ of Al $\simeq$ 4.2.
12. From breakdown voltage of metal insulator-metal junction, assuming ϕ of Al = 4.08.
13. Assuming ϕ of Ag = 4.31.
14. Hexagonal crystal structure.
15. Face-centered-cubic structure.
16. Assuming ϕ of Hg = 4.52.
17. Using various oxides, e.g., ϕ of PbO = 4.08.
18. Absolute work function value using photoemission-retarding potential method.
19. From breakdown of metal insulator-metal junction, assuming ϕ of Al = 4.08.
20. Monolayer on W substrate.
21. Also used contact potential shifts of two <211> Ta crystals to get low-temperature values of ϕ.
22. 15 layers.

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Emissive m

Oxides of:
Ba.....
Sr......
Ca......
Th.....

Hf.....
Zr......
Ti......
Sc......
Y......
La......
Ce.....
Pr......
Nd......
Sm.....
Eu......
Gd.....
Tb.....
Dy.....
Ho.....
Er.....
Yb....
Lu....
U.....
Hexaboric
Ca....
Sr.....
Ba....
Th....
Y.....
La.....
Ce....
Pr.....
Nd....
Gd....
Dy....
Ho....
Er.....
Yb....
Lu....
Tm...
Carbides
Ta....

Th...

Ti....
Zr....

U....
Si....
Hf...
V....
Mo...

Table 9j-2. Work Functions for Various Compounds

Emissive material	Base metal	Work function	Temperature range, K	Reference	Year
Oxides of:					
Ba	Pt	$1.4 + 7 \times 10^{-4} T$	700–950	1	1965
Sr	Pt	$1.6 + 7 \times 10^{-4} T$	1000–1180	1	1965
Ca	Pt	$1.86 + 7 \times 10^{-4} T$	1080–1380	1	1965
Th	W, Ta, Mo	$\sim2.6 + 2.4 \times 10^{-4} T$	~1300–2200	2, 3	1947-8
	Re, Nb	$2.37 + 4 \times 10^{-4} T$	1800–1700	4	1962
Hf	W	$2.82 + 4.72 \times 10^{-4} T$	1300–1950	5	1959
Zr	....	3.9	2000	6	1953
Ti	....	3.7	2000	6	1953
Sc	W	$3.66 + 2.2 \times 10^{-4} T$	1300–2000	5	1959
Y	Re, Nb	$2.9 + 1.6 \times 10^{-4} T$	1300–1700	4	1962
La	Ni	$3.0 + .075 \times 10^{-4} T$	~1000–1100	7	1959
Ce	....	$2.3 + 4.1 \times 10^{-4} T$	~1800–2000	6	1953
Pr	W	$2.8 + 5.4 \times 10^{-4} T$	~1400–1600	8	1958
Nd	W	$2.3 + 4.1 \times 10^{-4} T$	~1400–1600	8	1958
Sm	W	$2.8 + 5.1 \times 10^{-4} T$	~1700–1900	8	1958
Eu	W	$2.6 + 6 \times 10^{-4} T$	~1400–1600	8	1958
Gd	W	$2.1 + 4.5 \times 10^{-4} T$	1100–1600	8	1958
Tb	W	$2.1 + 5.4 \times 10^{-4} T$	1400–1600	8	1958
Dy	W	$2.1 + 4.16 \times 10^{-4} T$	1100–1600	8	1958
Ho	W	$2.3 + 5.1 \times 10^{-4} T$	1350–1950	8	1958
Er	W	$2.4 + 4.35 \times 10^{-4} T$	~1700–1900	8	1958
Yb	W	$2.7 + 2.85 \times 10^{-4} T$	1500–1900	8	1958
Lu	W	$2.3 + 6 \times 10^{-4} T$	~1500–1700	8	1958
U	W	$\sim3.1 + 2.1 \times 10^{-4} T$	1350–2100	9	1963
Hexaborides of:					
Ca	None	$2.86 + 3.8 \times 10^{-4} T$	1100–1400	10	1951
Sr	None	$2.67 + 5.82 \times 10^{-4} T$	1250–1459	10	1951
Ba	None	$3.45 + 1.74 \times 10^{-4} T$	1250–1650	10	1951
Th	None	$2.92 + 4.72 \times 10^{-4} T$	1150–1600	10	1951
Y	Ta	$2.2 + 1.8 \times 10^{-4} T$	....	11	1958
La	None	$2.66 + 1.23 \times 10^{-4} T$	1080–1300	10	1951
Ce	None	$2.59 + 3.0 \times 10^{-4} T$	1140–1370	10	1951
Pr	Ta	$3.46 - 7.9 \times 10^{-4} T$	....	11	1958
Nd	Ta	$3.97 - 1.08 \times 10^{-4} T$	....	11	1958
Gd	Ta	$2.05 + 4.28 \times 10^{-4} T$	....	11	1958
Dy	Ta	$3.53 + 1.37 \times 10^{-4} T$	....	11	1958
Ho	Ta	$3.42 + 1.86 \times 10^{-4} T$	....	11	1958
Er	Ta	$3.37 + 2.15 \times 10^{-4} T$	....	11	1958
Yb	Ta	$3.13 + 3.32 \times 10^{-4} T$	....	11	1958
Lu	Ta	$3.0 + 5.0 \times 10^{-4} T$	....	11	1958
Tm	W	$2.75 + 3.3 \times 10^{-4} T$	1100–1800	12	1964
Carbides of:					
Ta	W	$3.14 + 5.3 \times 10^{-4} T$	1400–2300	13	1951
	Ta	$3.17 + 5.4 \times 10^{-4} T$	1600–2250	14	1962
Th	Ta	$3.2 + 0.16 \times 10^{-4} T$	1500–2000	6	1958
	W	$3.5 - 1.32 \times 10^{-4} T$	1400–2300	13	1951
Ti	W	$3.35 + 1.35 \times 10^{-4} T$	1400–2300	13	1951
Zr	W	$2.18 + 5.1 \times 10^{-4} T$	1178–2073	13	1951
	W	$3.24 + 2.0 \times 10^{-4} T$	1800–2000	15	1962
U	W	$2.94 + 1.1 \times 10^{-4} T$	1200–2100	16	1960
Si	Ta	$3.5 + 0.5 \times 10^{-4} T$	....	6	1958
Hf	W	$3.42 + 1.75 \times 10^{-4} T$	1800–2000	15	1962
V	W	3.85	1800–2000	15	1962
Mo	None	$5.36 - 4 \times 10^{-4} T$	1400–1650	17	1967

TABLE 9j-2. WORK FUNCTIONS FOR VARIOUS COMPOUNDS (Continued)

Emissive material	Base metal	Work function	Temperature range, K	Reference	Year
Borides of:					
Ta(mono)	W	$2.89 + 2.14 \times 10^{-4}T$	1400–2100	13	1951
Ta(di)	W, Ta, C	~ 2.85	1600–1800	18	1962
Ta(di)	None	4.26	1100–1550	17	1967
Zr(mono)	W	$4.48 - 4.76 \times 10^{-4}T$	1500–2100	13	1951
Ti(di)	None	$4.6 - 1.17 \times 10^{-4}T$	1350–1850	19	1957
V(di)	None	$4.2 + 6.1 \times 10^{-4}T$	1450–1800	19	1957
Nb(di)	None	$4.0 + 3.65 \times 10^{-4}T$	1500–2000	19	1957
Cr(di)	None	$4.1 + 3.55 \times 10^{-4}T$	1450–1900	19	1957
Mo(di)	None	$3.85 + 4.9 \times 10^{-4}T$	1550–2050	19	1957
Hf(di)	HfC	~ 3.7	2240	20	1963
U(di)	W	$\sim 3.3 + .2 \times 10^{-4}T$	1300–2100	9	1963
U(tetra)	W	$\sim 3.4 - .8 \times 10^{-4}T$	1300–2100	9	1963
Y(tetra)	Ta	$3.2 + 2.5 \times 10^{-4}T$	1530–1890	21	1966
Gd(tetra)	Ta	$2.5 + 4.0 \times 10^{-4}T$	1560–1750	21	1966
Silicides of:					
Re(di)	W	$4.02 - 2.67 \times 10^{-4}T$	1200–1400	22	1966
Nb(di)	W	$4.34 - 5.25 \times 10^{-4}T$	1800–1700	22	1962
Zr(di)	W	$3.95 - 5.0 \times 10^{-4}T$	1200–1900	22	1962
V(di)	W	$3.26 - 7.5 \times 10^{-4}T$	1100–1600	22	1962
Cr(mono)	W	$3.49 - .58 \times 10^{-4}T$	1200–1400	22	1962
Cr(di)	W	$3.78 - 1.2 \times 10^{-4}T$	1200–1450	22	1962
U(di)	W	$3.0 + 2.1 \times 10^{-4}T$	1300–2000	9	1963
U(tri)	W	$3.22 + 1.1 \times 10^{-4}T$	1300–2000	9	1963
W(di)	None	~ 4.62	1350–1610	17	1967
Ta(di)	None	~ 4.71	1180–1600	17	1967
Mo(di)	None	~ 4.73	~ 1500	17	1967
Nitrides of:					
Zr	W	3.96	2000	13	1951
B	W	4.0	2000	13	1951
Ti	W	3.96	2000	13	1951
U	W	$\sim 3.1 + 2.14 \times 10^{-4}T$	1350–2100	9	1963

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9j-2. Secondary
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electrons through
depends on the pri
with respect to th
surface conditions
selected to be rep

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imum denoted by
occurs is listed as
electrons are exoit
unable to diffuse
decreases as the p
the secondary emi
over, respectively,

In general, low
insulators. Roug
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parts of the rough
vacuum. A good
as soot.

The highest sec
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cepts have been r
ratio. One appro
near the surface so
The resulting seco
increase over that

A number of re
9j-3 is taken from

1 See, for exampl
R. Kollath, "Ha
ladungen, Springer
O. Hachenberg
Electron Phys. 11,
H. Bruining, "P
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9j-2. Secondary Emission Measurements. The secondary emission ratio δ of a material is the number of secondary electrons emitted on the average, per incident primary electron. Secondary electron emission involves three processes: (1) the excitation of electrons in the solid by the incident primary electron beam, (2) the diffusion of the excited electrons to the surface, and (3) the escape of the excited electrons through the surface barrier. The secondary emission ratio of a given surface depends on the primary electron energy, the angle of incidence of the primary electrons with respect to the surface, bulk properties of the material, and most important, the surface conditions. In so far as practicable, yield measurements given here have been selected to be representative of clean surfaces at normal incidence.

The secondary emission ratio increases with primary energy until it reaches a maximum denoted by δ_m in Table 9j-3. The primary energy at which this maximum occurs is listed as $E_{p,max}$. When the primary energy is raised beyond the maximum, electrons are excited increasingly deeper within the material so that many of them are unable to diffuse to the surface. The secondary emission ratio therefore slowly decreases as the primary energy is increased beyond $E_{p,max}$. The voltages for which the secondary emission ratio crosses the $\delta = 1$ line are called the *first* and *second crossover*, respectively, and are designated as E_I and E_{II} in the table.

In general, lower secondary emission ratios are obtained from metals than from insulators. Roughening the surface of a material or increasing its porosity will further decrease the secondary emission ratio since the secondary electrons intercept other parts of the roughened and porous surface and are prevented from escaping into the vacuum. A good example of such a low secondary emission surface is carbon deposited as soot.

The highest secondary emission yields have been previously obtained from alkali halides and various oxides, such as NaBr or MgO. However, certain solid-state concepts have been recently employed to substantially increase the secondary emission ratio. One approach using Cs-treated GaP depends on bending the energy bands near the surface so that the effective electron barrier for escaping secondaries is lowered. The resulting secondary emission ratio for this surface represents an order of magnitude increase over that previously achieved from "natural"-appearing compounds.

A number of reviews of secondary emission have recently been published.[1] Table 9j-3 is taken from the review by Whetten except for a few additions.

[1] See, for example:

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TABLE 9j-3. Secondary Emission Parameters

Elements	δ_{max}	$E_{p,max}$	E_I	E_{II}	References
Ag	1.5	800	200	>2000	1, 2, 3
Al	1.0	300	300	300	2
Au	1.4	800	150	>2000	1, 2, 3
B	1.2	150	50	600	5
Ba	0.8	400	None	None	2
Be	0.5	200	None	None	2, 6, 7, 4
Bi	1.2	550	...	......	8, 9
C (diamond)	2.8	750	...	>5000	10
(graphite)	1.0	300	300	300	11
(soot)	0.45	500	None	None	11
Cd	1.1	450	300	700	12, 4
Co	1.2	600	200		13, 14
Cs	0.7	400	None	None	2, 15
Cu	1.3	600	200	1500	1, 12, 2
Fe	1.3	400	120	1400	14, 3, 16
Ga	1.55	500	75	......	17
Ge	1.15	500	150	900	5, 18, 9
Hg	1.3	600	350	>1200	17
K	0.7	200	None	None	19, 20
Li	0.5	85	None	None	2
Mg	0.95	300	None	None	15, 2
Mo	1.25	375	150	1200	1, 21, 3, 22, 16
Na	0.82	300	None	None	24
Nb	1.2	375	150	1050	1, 3
Ni	1.3	550	150	>1500	1, 14, 13, 21, 16
Pb	1.1	500	250	1000	8, 17
Pd	>1.3	>250	120	......	24
Pt	1.8	700	350	3000	3
Rb	0.9	350	None	None	19
Sb	1.3	600	250	2000	25
Si	1.1	250	125	500	5
Sn	1.35	500	...	......	8, 23
Ta	1.3	600	250	>2000	1
Th	1.1	800	...	......	2
Ti	0.9	280	None	None	11
Tl	1.7	650	70	>1500	9
W	1.4	650	250	>1500	26, 1, 27, 3
Zr	1.1	350	...	......	11

Alkali h
  CsCl..
  KBr(o
  KCl(cr
    (la
  KI(cry
    (lay
  LiF(or
    (la
  NaBr(
    (l
  NaCl(o
    (l
  NaF(or
    (la
  NaI(or
    (lay
  RbCl(la
Oxides:
  Ag_2O...
  Al_2O_3(la
  BaO(lay
  BeO....
  CaO....
  Cu_2O...
  MgO(or
    (la
  MoO_2...
  SiO_2(qua
  SnO_2...
Sulfides:
  MoS_2...
  PbS....
  WS_2.....
  ZnS.....
Others:
  BaF_2(lay
  CaF_2(lay
  $BiCs_3$...
  $BiCs$....
  $GeCs$....
  Rb_3Sb...
  $SbCs_3$....
  Mica(nat
    (syn
  Glasses..
  MgF_2....
  Talc.....
  Teflon...
  $ZnSiO_4$...
  GaP + C
Phosphors:
  P_1.......
  P_2.......
  P_3.......
  P_4.......

* Maximum

TABLE 9J-3. SECONDARY EMISSION PARAMETERS (*Continued*)

References
1, 2, 3
2
1, 2, 3
5
2
2, 6, 7, 4
8, 9
10
11
11
12, 4
13, 14
2, 15
1, 12, 2
14, 3, 16
17
5, 18, 9
17
19, 20
2
15, 2
1, 21, 3, 22, 16
24
1, 3
1, 14, 13, 21, 16
8, 17
24
3
19
25
5
8, 23
1
2
11
9
26, 1, 27, 3
11

Compounds	δ_{max}	$E_{p,max}$	Reference
Alkali halides:			
CsCl	6.5	....	28
KBr(crystal)	14	1800	29, 30
KCl(crystal)	12	1600	31, 32
(layer)	7.5	1200	31, 33
KI(crystal)	10	1600	29, 32, 30
(layer)	5.6	....	28
LiF(crystal)	8.5	....	34
(layer)	5.6	700	28
NaBr(crystal)	24	1800	35, 32
(layer)	6.3	....	28
NaCl(crystal)	14	1200	36, 30, 29, 32, 34
(layer)	6.8	600	28, 37
NaF(crystal)	14	1200	34
(layer)	5.7	....	28
NaI(crystal)	19	1300	34
(layer)	5.5	....	28
RbCl(layer)	5.8	....	28
Oxides:			
Ag₂O	1.0	....	38
Al₂O₃(layer)	2-9	....	39, 40, 36, 2
BaO(layer)	2.3-4.8	400	40, 2
BeO	3.4	2000	40
CaO	2.2	500	40
Cu₂O	1.2	400	28, 41
MgO(crystal)	20-25	1500	42, 43, 44, 45
(layer)	3-15	400-1500	40, 46, 47, 42
MoO₂	1.2	....	38
SiO₂(quartz)	2.1-4	400	39, 40
SnO₂	3.2	640	48
Sulfides:			
MoS₂	1.1	....	28
PbS	1.2	500	31
WS₂	1.0	....	28
ZnS	1.8	350	49
Others:			
BaF₂(layer)	4.5	....	28
CaF₂(layer)	3.2	....	28
BiCs₃	6	1000	31
BiCs	1.9	1000	31
GeCs	7	700	31
Rb₃Sb	7.1	450	31
SbCs₃	6	700	31, 50
Mica(natural)	2.4	350	39
(synthetic)	2.9	800	51
Glasses	2-3	300-450	39, 52
MgF₂	4.0	400	51
Talc	2.3	300	51
Teflon	1.7	600	53
ZnSiO₄	2.6	300	53
GaP + Cs	120*	2500*	54
Phosphors:			
P₁	2.7	750	55
P₂	3.4	750	55
P₃	3.9	1000	55
P₄	3.7	700	55

* Maximum voltage measured was 2500 volts, δ was still rising.

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Appendix B

Electronic Work Function of Melts of Na-K-Cs and Na-K-Rb Ternary Systems

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ABSTRACT

Wide use of alkali metals and their alloys in modern technology requires knowledge their physicochemical properties. In this paper we present the results of the experimental study of temperature and composition dependencies of electronic work function (EWF) of ternary alloys of the Na-K-Cs and Na-K-Rb systems, as well as Na-Cs and K-Cs binary alloys. Polytherms of EWF $\varphi(T)$ are linear with negative or positive temperature coefficients (TC) for the Na-K-Rb and Na-K-Cs systems over the temperature range from 300 to 420K. No extremums were found on the EWF isotherms at 298K, constructed as curves of equal values of EWF over the entire area of the composition triangle (isothermal surface).

INTRODUCTION

Study of the electronic work function (EWF) of alkali metals and their multicomponent alloys is of great importance in photoemission theory, in creating new power-intensive chemical current sources, highly effective photocathodes and charged particles sources, and so on [1,2]. An analysis of literature showed that the temperature and composition dependencies of EWF of such materials are studied insufficiently. For instance, the EWF of ternary alloys of alkali metals is not studied well enough [3,4].

TECHNIQUE FOR ELECTRONIC WORK FUNCTION MEASURMENT

The work function was measured by the Fowler's photoelectric method, which yields an experimental error of about 1%. Automatic processing of the photocurrent data with a computer program ensured proper alignment of the experimental spectral dependencies with theoretical Fowler's curves.

The alloys were prepared using high purity metals with 99.995% content of the base element. Experiments were performed under 10^{-7} Pa vacuum condition in a completely sealed metered cell, constructed specifically for the study of EWF of alkali metals and their multicomponent melts [5]. Measurements were performed in steps of 1 to 3 degrees in the temperature range from 20 to 120°C. At each temperature the alloys were allowed to settle for at least half an hour in order for all possible structure transformations to complete.

RESULTS AND DISCUSSION

In this work, the experimental results on the electronic work function of 110 ternary alloys of the Na-K-Cs system and 40 ternary alloys of the Na-K-Rb system are presented. The ternary alloys were prepared by adding K to the initial Na-Cs binary alloy at constant

X_{Na}:X_{Cs} ratio. The compositions of the studied alloys of the Na-K-Cs system are shown in Fig 1.
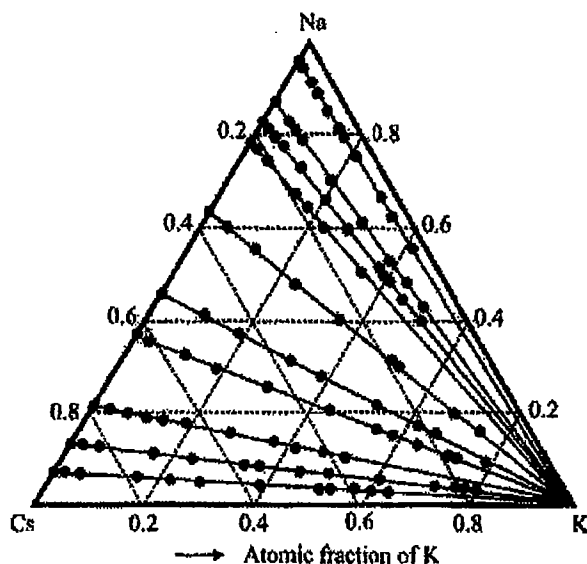
Fig 1. Compositions of the 110 ternary alloys of the Na-K-Cs system along the sections, for which the electronic work function was measured.

The studied alloys, formed along ten sections, cover the entire composition triangle. Polytherms of EWF of alloys over the studied temperature ranges are described by linear equations with positive or negative TC, depending on the composition of an alloy. For the alloys formed along the section with ratio X_{Na}:X_{Cs} = 1:11 and with 2.0 at.% content of K, the isotherms of EWF have a positive TC, equal to $3.4 \cdot 10^{-4}$ eV/K, while for other alloys along the same section the TC are negative.

Absolute values of TC for the alloys, prepared along the sections with X_{Na}:X_{Cs} = 6:1 and X_{Na}:X_{Cs} = 1:1, exhibit negative deviations from the additive curve. TC values increase when the content of Na in the ternary alloys increases. The positive TC of the polytherms for some Na-K-Cs and Na-K-Rb alloys may be explained by desorption of a surface-active component with increasing temperature.

In ternary alloys rich with Na the EWF decreased, when up to 20 at.% of K was added. However, if Na is replaced by Cs in the ternary alloys, K becomes a surface-inactive component. One can note, that addition of K to the Na-Rb alloys results in the increase of a photocurrent by an order of magnitude The isotherms of the EWF of Na-K-Cs alloys with constant X_{Na}:X_{Cs} ratio at 313K are shown in Fig.2. The isotherms do not exhibit any extremums. The polytherms of EWF of the studied binary alloys were also obtained. For all

Na-Rb alloys and Cs-rich Na-Cs and K-Cs alloys they are satisfactorily described by linear equations with negative TC. Temperature coefficients are positive for alloys containing small amounts of Cs due to desorption of Cs from the surface layer with increasing temperature. The concentration dependencies of the temperature coefficients of the EWF for alloys are complicated: their absolute values reveal a large scatter and oscillations. With increasing temperature, the changes in EWF appear to depend on two factors. Firstly, structural changes weaken interatomic bonds and reduce the electrical barrier on the surface layer. Secondly, the surface layer composition changes due to desorption of the surface-active component.
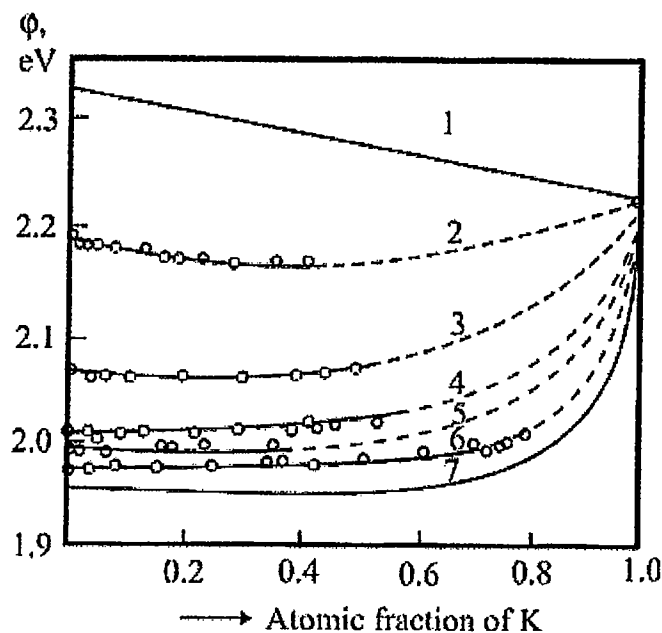
Fig.2. Isotherms of electronic work function at 313K for alloys: 1 - Na-K; 2 – $X_{Na}:X_{Cs}=58:1$; 3 - 14:1; 4-6:1; 5-4:1; 6-1:11; 7-Cs-K.

The first factor leads to a reduction of the EWF, while the second results in an increase of the EWF of the alloys. Cs is a surface-active component in the Na-Cs and K-Cs systems. Therefore, if the bulk concentration of Cs is small, its concentration in surface layer decreases sharply with increasing temperature, leading to an increase of the EWF. If the bulk concentration of Cs reaches 15-20 at.%, the desorption of Cs has only a slight influence on the composition of the surface layer, resulting in an increasing role of the structure factor.

More detailed study of the EWF of the Na-Cs system with 0 to 50 at.% content of Cs revealed a complicated character of the EWF isotherm at -90°C in the range of Cs concentration from 0 to 15 at.%. Our results do not exhibit a minimum near 32.4 at.% Cs. The K-Cs system has a phase diagram with an azeotropic minimum, so one would expect

appreciable changes in the EWF in the range of small concentrations of the components (Fig 3).

Addition of up to 25-30 at. % of Cs results in a decrease of the EWF to a value close to that of a pure Cs (~1.95 eV). Further addition of Cs does not change EWF values of the alloys. More detailed study of the EWF in the concentration ranges 0 - 20 at.% and 70 - 100 at.% of Cs showed that addition of up to 2 at.% of Cs to K leads to EWF values sharply decreasing toward that of a pure Cs. Our results are in satisfactory agreement with theoretical calculations performed using the electron density functional method [6].

The curves of the equal EWF values (isolines) for the Na-K-Cs alloys at 298K are presented in Fig.3.
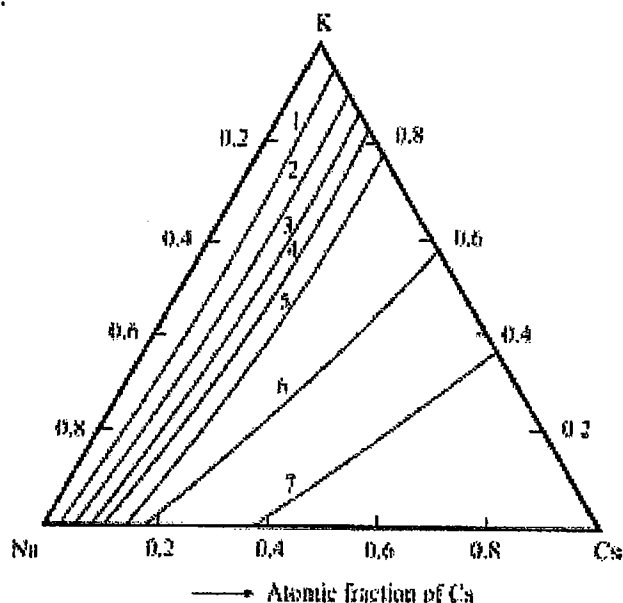
Fig.3 Curves of equal values of the EWF of the Na-Cs-K alloys at 298 K: 1 - 2,15; 2 - 2,04; 3 - 2,02; 4 - 2,00; 5 - 1,98; 6 - 1,97; 7 - 1,96 eV. Values of the EWF for Na, K and Cs at 298K are 2.41, 2.28 and 1.95 eV, respectively.

CONCLUSION

Polytherms of the EWF for the Na-Cs-K and Na-Rb-K systems over the studied temperature range are described by linear equations with positive and negative temperature coefficients. The temperature and concentration dependencies of the EWF of the Na-Cs and K-Cs alloys were measured. No extremums were found on the EWF isotherms of the Na-Cs system at -90°C, and the Na-Cs-K and Na-Rb-K systems at 298K.
Our results showed both absence of any extremum in the concentration dependence of the EWF for systems with eutectic alloys and the effect of chemical composition on the shape of a EWF isotherm at low temperatures only.

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Appendix C

HANDBOOK OF
PHYSICS

Prepared by a staff of specialists

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Chapter 6

Thermionic Emission

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Introduction

Thermionic emission as it is understood today is that branch of physics having to do with the various phenomena connected with the ejection of electrons or positive ions from a solid when it is heated to a sufficiently high temperature. The study of this subject had its meager and floundering beginning over two hundred years ago when it was discovered that air in the neighborhood of hot solids could conduct electricity. It was gradually learned that the hot bodies emitted charged particles. A notable step forward was made by J. J. Thomson, who showed that the charged particles which were emitted by carbon at fairly high temperatures and in a partial vacuum were predominantly electrons. The important advances in the subject from this time on were closely tied to the degree of perfection of high-vacuum techniques. As it became possible to make measurements in better and better vacuums, effects of gas and surface contamination on the emission phenomena could be eliminated and the essential features of true thermionic emission could be investigated. The evolution of the field was greatly enhanced by the development of the quantum theory of the behavior of electrons in solids. At present the basic phenomena in electron and positive ion emission from essentially pure metals are well understood. Though significant advances have been made in the understanding of electron emission from composite materials such as the alkaline earths, the state of development is not as complete as for the pure metals.†

It is advantageous to divide the field into the following categories: the electron and ion emission from uniform pure metal crystals, the electron emission from polycrystalline metals, and the emission from metals with various adsorbed monolayers.

1. Uniform Pure Metal Crystals

Thermionic-emission Equation for Electrons. The current density j of electrons emitted from a uniform surface of a pure metal can be expressed in terms of the metal temperature T by the equation

$$j = A(1 - r)T^2 e^{-\phi/kT} \tag{6.1}$$

† For a good bibliography and critical treatment of electron emission from metals, see the article on thermionic emission by Conyers Herring, *Revs. Mod. Phys.*, **21**: 185 (1949).

This equation is the fundamental equation of thermionic emission and is usually known as the Richardson equation. The equation can be derived either from thermodynamical [1]† arguments or from the application of statistical mechanics [2] in connection with the quantum mechanics of electrons in metals.

Here A is a constant composed of a combination of fundamental physical constants

$$A = \frac{4\pi m k^2 e}{h^2} = 120 \text{ amp/cm}^2 \cdot \text{deg}^2 \tag{6.2}$$

where e is the absolute value of the electronic charge, k is Boltzmann's constant, and h is Planck's constant. r is a reflection coefficient for electrons crossing the potential barrier at the metal surface when the electric field just outside the metal surface is zero. It is possible that r could change somewhat with the temperature but it is thought that the quantity $1 - r$ is rather insensitive to temperature changes. For pure metals r is of the order 0.05. The reflection coefficient r will also depend slightly on the component of the electric field at the surface of the metal. This will be discussed in more detail under the section on the Schottky effect. ϕ is usually called the electronic work function and is defined so that ϕe is a characteristic amount of work required to remove an electron from the interior of the metal to a position just outside of the metal. In general ϕ is dependent to some extent on temperature and the normal component of electric field at the metal surface. Some experimentally determined values of ϕ for clean metals are given in Table 6.1. Since the emitted current density j depends on ϕ exponentially, small variations of ϕ caused by changes in temperature or electric field produce significant changes in j.

The current density given by Eq. (6.1) will not necessarily be that found by measuring the current to a plane electrode parallel to the surface of the hot metal because of the negative space charge produced between the two electrodes. Under some conditions this produces an electric field near the metal surface which retards the emitted electrons and causes the low-energy electrons to return to the surface. Care must be taken to make the potential difference such that no electrons are returned to the hot metal in order to obtain the current j given by the emission formula. If the potential difference is made too high, the field thus produced outside the metal surface

† Numbers in brackets refer to References at end of chapter.

changes the work function and the reflection coefficient as indicated above.

Statistical Derivation of the Richardson Equation. According to the modern quantum theory of electrons in metals [3], the outermost electrons in the atoms of which the metal is constituted are almost free to move through the metallic lattice. There exist certain discrete energy states which these electrons may occupy. These are represented schematically in Fig. 6.1. The number of such states in any
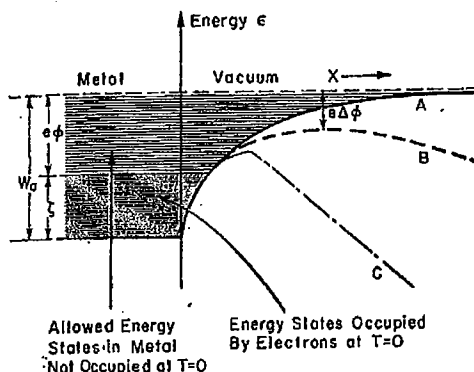

Fig. 6.1. Energy levels in a metal and potential energy of an electron near the metal surface.

energy interval is so large that the energy states are densely packed. The number of energy states dN which have energy between ϵ and $\epsilon + d\epsilon$ is

$$dN = 2\pi(2m)^{3/2}h^{-3}\epsilon^{1/2}\,d\epsilon \qquad (6.3)$$

The rather freely moving electrons which occupy these energy states are prevented from escaping from the metal by electrical forces at the surface of the metal. The potential energy of an electron due to the action of these forces is shown as a function of its distance away from the surface in Fig. 6.1 by curve A. It is assumed that there is no applied electric field at the surface nor fields due to space charge. From very near the surface to large distances away the potential energy of an electron is largely due to the image force $-e^2/2x^2$ and is essentially $W_a - (e^2/4x)$.

The Fermi distribution function [4] gives the number of electrons per unit volume in the metal and the manner in which they are distributed over the allowed energy states. This function is

$$f = \frac{1}{1 + e^{(\epsilon-\zeta)/kT}} \qquad (6.4)$$

where ϵ is the energy of a particular allowed state measured from the bottom of the conduction band (see Fig. 6.1). ζ is the energy below which all energy states are occupied by electrons at the absolute zero of temperature. ζ is consequently dependent on the number of electrons per unit volume in the conduction band at $T = 0$. Thus at $T = 0$, $W_a - \zeta = e\phi$. ζ is slightly dependent on temperature. The Fermi function f gives the probability that at temperature T the state of energy ϵ will be occupied. Therefore

the probable number of electrons dn per unit volume occupying states between ϵ and $\epsilon + d\epsilon$ at temperature T is

$$dn = 2f(\epsilon)\,dN \qquad (6.5)$$

The factor 2 comes from the fact that two electrons may occupy each energy state, one electron with spin in one direction and the other with spin in the opposite direction. Consequently at $T = 0$

$$n = 2\int_0^{\zeta} dN = \frac{8\sqrt{2}\pi m^{3/2}}{h^3}\int_0^{\zeta}\epsilon^{1/2}\,d\epsilon$$

$$= \frac{16\sqrt{2}\pi m^{3/2}}{3h^3}\zeta^{3/2} \qquad (6.6)$$

Knowing the value of ζ at $T = 0$ is equivalent to knowing the number of electrons per unit volume in the metal. Since $\epsilon = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$, the number of energy states corresponding to velocity ranges dv_x at v_x and so on is

$$dN = \frac{m^3}{h^3}\,dv_x\,dv_y\,dv_z \qquad (6.7)$$

Hence the probable number of electrons in this velocity range is

$$dn = 2f(\epsilon)\frac{m^3}{h^3}\,dv_x\,dv_y\,dv_z \qquad (6.8)$$

With the help of this expression and Eq. (6.4) the electron current emitted per unit area of the metal is

$$j = \frac{2m^3}{h^3}e\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \frac{T(v_x)v_x\,dv_x\,dv_y\,dv_z}{\exp\left[\dfrac{\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) - \zeta}{kT}\right] + 1} \qquad (6.9)$$

where $T(v_x)$ is the probability that an electron approaching the potential barrier at the metallic surface with velocity v_x will pass through or over the barrier. Evaluating the integrals over v_y and v_z, the current density is

$$j = \frac{4\pi m^2 ekT}{h^3}$$

$$\int_0^{\infty} T(v_x)\log\left[1 + \exp\left(-\frac{\frac{1}{2}mv_x^2 - \zeta}{kT}\right)\right]v_x\,dv_x \qquad (6.10)$$

It is necessary to discuss the nature of $T(v_x)$ and this requires a knowledge of the form of the potential energy barrier at the surface. Consider the case where the force acting on the electron is due to the image forces and an applied electric field E. The potential energy of an electron at a distance x from the metal surface can then be written as

$$W(x) = W_a - \frac{e^2}{4x} - eEx \qquad x > 0 \qquad (6.11)$$

$W(x)$ is represented as curve B in Fig. 6.1. If one neglects the wave properties of an electron, then the

only electrons contributing to the emitted current would be those which have sufficient velocity in the x direction to get over the barrier or those for which

$$\tfrac{1}{2}mv_x^2 \geq W_a - e\,\Delta\phi \qquad (6.12)$$

From Eq. (6.11) $\Delta\phi = \sqrt{eE}$. For this model all electrons obeying (6.12) are transmitted and all others are reflected so that

$$T(v_x) = 1 \quad \text{for } v_x \geq \sqrt{\frac{2(W_a - e\,\Delta\phi)}{m}} \qquad (6.13a)$$

$$= 0 \quad \text{for } v_x < \sqrt{\frac{2(W_a - e\,\Delta\phi)}{m}} \qquad (6.13b)$$

Actually, however, even for condition (6.13a) there will be a small amount of reflection due to the fact that an electron with sufficient energy to be emitted will come too close to one or more atoms of the metal and be backscattered. To take account of this, we put

$$T(v_x) = 1 - r \quad \text{for condition (6.13a)}$$
$$= 0 \quad \text{for condition (6.13b)}$$

Furthermore, it will be assumed that over the important range of v_x, r is independent of v_x. r is the reflection coefficient already discussed in connection with Eq. (6.1). The current density is

$$j = \frac{4\pi m^2 ekT}{h^3}(1 - r)$$
$$\int_{v_{x0}}^{\infty} \log\left[1 + \exp\left(-\frac{\tfrac{1}{2}mv_x^2 - \zeta}{kT}\right)\right] v_x\,dv_x$$

where v_{x0} is the expression in (6.13b). For values of T and v_x of interest the second term in the logarithm is small compared to 1 and a sufficiently precise evaluation of the integral can be obtained by using the final term in the expansion of the log term. Using Eq. (6.12) and $e\phi = W_a - \zeta$, the current density is

$$j = A(1 - r)T^2 \exp\left(-\frac{e\phi - e\sqrt{eE}}{kT}\right) \qquad (6.14)$$

where A has the value (6.2). This equation is the same as Eq. (6.1), when the applied electric field E is zero.

The Thermionic Work Function ϕ. The work functions of most metals have been determined experimentally from the thermionic-emission current or from a measurement of the frequency threshold for the photoelectric emission from the metal surface in question. Theoretical methods of calculating the work function of a metal are still not accurate enough to furnish reliable values. The customary way of determining the work function is to measure the emission current at a fixed temperature T for a range of applied fields E and extrapolate this curve to $E = 0$ in order to determine the emission current appropriate for zero field. This procedure is repeated for a range of temperatures and the current densities so measured divided by T^2 are plotted against $1/T$. The slope of this curve is the apparent work function. The analytical statement of this is

$$\phi^* = -\frac{k}{e}\frac{d(j/T^2)}{d(1/T)} \qquad (6.15)$$

For a uniform surface Eq. (6.1) applies so that

$$\phi^* = \phi - T\frac{d\phi}{dT} - \frac{kT^2}{e}(1 - r)\frac{dr}{dT} \qquad (6.16)$$

Thus the apparent work function as measured from the slope is equal to the true work function only when ϕ or r are independent of temperature. As already stated, r is small and insensitive to temperature changes for clean metals. The term $T(d\phi/dT)$ is not as certain. It is likely to be small for clean metals with a uniform surface but not negligible. From some attempts to measure the magnitude of this term for Ta, W, and Mo it appears likely that it is about 0.1 ev. It can be much larger than this for surfaces covered with monolayers or for surfaces of semiconductors.

Experiment has shown that the work function for a given metal single crystal depends on the particular crystal surface from which electron emission is taking place. Such a difference is to be expected because the arrangement of metal atoms on the surface differs with the different exposed crystallographic planes and this in turn would make the forces acting on an electron near the surface somewhat different. Table 6.1 shows the difference in the apparent work function of Cu, Ag, and W as a function of the exposed crystal surface. It will be seen that the differences become as high as 0.25 ev.

TABLE 6.1. WORK FUNCTION FOR SINGLE CRYSTAL SURFACES

Element	Index of crystal direction of normal to surface	Work function, ev
Cu	111	4.89
	100	5.64
Ag	111	4.75
	100	4.81
W	112	4.50
	310	4.30

Velocity Distribution of Emitted Electrons. It was demonstrated originally by Richardson that the electrons emitted from a hot metal possess a Maxwellian distribution of velocities. This is the case even though the velocity distribution law inside the metal is that of Fermi, i.e., (6.8), or

$$dn = \frac{2m^3}{h^3}\frac{dv_x\,dv_y\,dv_z}{\left[1 + \exp\frac{\tfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2) - \zeta}{kT}\right]}$$

Let the velocities of the electrons outside the metal be v'_x, v'_y, v'_z. These will be related to the velocity

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$$\tfrac{1}{2}mv'^2_x = \tfrac{1}{2}mv_x^2 - W_a \qquad v'_y = v_y \qquad v'_z = v_z$$

provided the transmission coefficient is such that

$$T'(v_x) = 0 \qquad v_x < \sqrt{\frac{2W_a}{m}}$$

$$= 1 - r \qquad v_x \geq \sqrt{\frac{2W_a}{m}}$$

The number of electrons emitted per unit time whose velocities inside the metal lie in the range $v_x + dv_x$, etc., is

$$dn_0 = (1 - r)\,\frac{2m^3}{h^3}\,\frac{v_x\,dv_x\,dv_y\,dv_z}{1 + \exp\left[\dfrac{\tfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2) - \zeta}{kT}\right]}$$

$$v_x > \sqrt{\frac{2W_a}{m}}$$

The number of electrons emitted per unit time whose velocities outside the metal lie in the range $v'_x + dv'_x$, etc., is

$$dn' = (1 - r)\,\frac{2m^3}{h^3}$$

$$\frac{v'_x\,dv'_x\,dv'_y\,dv'_z}{1 + \exp\left[\dfrac{\tfrac{1}{2}m(v'^2_x + v'^2_y + v'^2_z) + e\phi}{kT}\right]} \qquad v'_x > 0$$

Since $e^{\epsilon\phi/kT} \gg 1$, the distribution law for emitted electrons is

$$dn' = (1 - r)\,\frac{2m^3}{h^3}\,e^{-\epsilon\phi/kT}$$

$$\exp\left[-\frac{\tfrac{1}{2}m(v'^2_x + v'^2_y + v'^2_z)}{kT}\right]v'_x\,dv'_x\,dv'_y\,dv'_z$$

(6.17)

This is the same distribution function that would have been obtained if the electrons inside the metal had been distributed in the velocity ranges according to Maxwell's law.

Field Effects. An electric field in the neighborhood of the surface of a clean metal which exhibits only one crystal face may exist most commonly because of a potential difference applied between the metal surface and a neighboring electrode or may exist because of the charge produced by electrons emitted into the space near the hot metal. Usually the field in the neighborhood of the surface during electron emission arises from both causes. For very low applied fields and appreciable electron emission the space-charge field in the neighborhood of the cathode is such as to repel many of the electrons emitted with the lower energies. For applied fields high enough to overcome the space-charge fields, all electrons emitted can be collected on a collecting electrode. At a constant emitter temperature the emission current will increase as the applied field increases in accordance with Eq. (6.14) if the applied field does not become too high (of the order 10^5 volts/cm). This increase in emission current is called the *Schottky effect* and is due to the lowering of the

potential barrier. The validity of Eq. (6.14) is usually tested by plotting log j against $E^{1/2}$ at constant emitter temperature. This is a straight line and is called the *Schottky line*.

Except for small periodic deviations of the emission current from the Schottky line, the theory is very well substantiated by experiment. The small periodic deviations of the emission current from that predicted by the Schottky theory are also a field effect but come about through the interference effect of electron waves as the shape of the barrier is changed by means of the applied field. This effect is superposed on the lowering of the barrier due to the applied field, which is just the usual Schottky effect. The periodic deviation is an interference phenomenon [5] analogous to that which would occur in the case of transmissions of light through a medium with a continuously varying index of refraction. This theory leads to the conclusion that the reflection coefficient r in Eq. (6.14) depends on the field E. The actual dependence on E is complicated in form. The main feature of the dependence of r on E is that r is an oscillatory function of E whose amplitude and period increase as E increases.

A still different field effect sets in for really high fields of the order 10^5 volts/cm and greater. For such high fields the potential barrier looks more like curve C in Fig. 6.1, and the barrier thickness begins to approach the order of magnitude of a wavelength of the most energetic electrons in the metal. In this case some electrons tunnel through the barrier, and the dependence of the emitted current on temperature and field is entirely different from that portrayed by Eq. (6.14). Under these conditions the emission is referred to as "field emission" and is not properly thermionic emission.

For the case of small applied fields produced by applying a potential difference between a plane emitter and a plane collecting anode such that the space charge of the emitted electrons nevertheless produces a retarding field near the emitter surface, the electrostatic potential between the planes is depicted in curve I (Fig. 6.2). The minimum in the potential at a distance of d_m from the emitter surface is caused by the negative space charge produced by the emitted electrons. Since the emitted electrons have a Maxwellian distribution (see section above on velocity distribution of emitted electrons), not
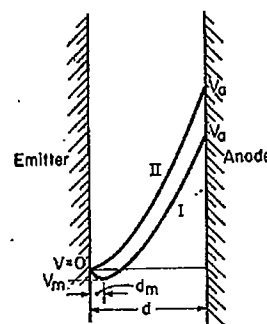

FIG. 6.2. Electric potential between an electron emitter and an anode.

all of the emitted electrons will have energy enough to overcome the potential minimum V_m and will return to the emitter. Consequently, the current density at the anode will be less than that given by the emission equation (6.1). Calling the emission current density given by Eq. (6.1) the saturation current and denoting it by j_s, Langmuir [6] has derived the relation between the actual current density j at the anode whose potential is V_a with respect to the emitter (emitter potential zero) and located a distance d from the emitter, as shown in Fig. 6.2

$$j = \frac{\sqrt{2e/m}}{9\pi} \frac{(V_a - V_m)^{3/2}}{(d - d_m)^2}$$

$$\left[1 + \frac{2.658\sqrt{kT}}{\sqrt{e(V_d - V_m)}} \right] \quad (6.18a)$$

$$V_m = \frac{-kT}{e} \log \frac{j_s}{j} \quad (6.18b)$$

$$d_m = \frac{\xi(V_a - V_m)}{4(\pi/2kT)^{1/4} m^{1/4} \sqrt{ej}} \quad (6.18c)$$

Knowing the saturated emission current density j_s, the difference of potential between emitter and anode, and their distance d apart, the equations above determine j, the actual anode current. The function $\xi(V_a - V_m)$ is a slowly varying function of $V_a - V_m$ and is tabulated in ref. [6]. However

$$2 < \xi < 2.55 \quad \text{for} \quad 7 < \frac{j_s}{j} < \infty$$

so that for considerable range of currents ξ can be taken as 2.5. Since $d_m/d \ll 1$ in most cases, Eq. (6.18a) does not depend sensitively on d_m anyway. When d_m and V_m can be neglected compared with d and V_a and when

$$\frac{2.66\sqrt{kT}}{\sqrt{eV_d}} \ll 1$$

the anode current is given by

$$j = \frac{\sqrt{2e/m}}{9\pi} \frac{V_a^{3/2}}{d^2} \quad (6.19)$$

which is known as *Child's law*.

Expressions for the space-charge limited current for other geometrical arrangements of emitter and anode have been worked out [7].

Emission of Positive Ions. When metals are heated to sufficiently high temperatures, they emit positive ions. At the lower part of the temperature range the ions are usually impurities contained in the metal or its surroundings such as the tube wall, etc. However, mass spectrographic studies show that at high enough temperatures the metal emits positive ions of the metal itself. The ratio of the number of singly charged metal ions to the number of neutral atoms evaporated is small.

A thermodynamical [8] and statistical [9] theory of metallic ion emission shows that the emitted ion current density is related to the temperature as follows

$$J_+ = \frac{2\pi ke M}{h^3} (1 - r) T^2$$

$$\exp \left(- \frac{e\phi_+}{kT} - \frac{1}{k} \int_0^T \frac{dT}{T^2} \int_0^T C_{pm}\, dT \right)$$

where C_{pm} is the heat capacity, at constant ⎸ of an ion in the condensed state, ϕ_+ is the ion work function, and r is a reflection co⎸ Except for a factor 2 multiplying the right-h⎸ and the additional term containing the speci⎸ of the ion in the solid, Eq. (6.20) would h⎸ same form as Eq. (6.1) for electron emissio⎸ specific heat term is missing in the electron e⎸ case because electrons distributed among the states according to the Fermi law contribute ⎸ negligible amount to the specific heat of th⎸ The factor 2 comes about because of a differ⎸ statistical weight.

The most precise and careful measureme⎸ positive-ion emission have been made on ⎸ denum [10]. When necessary precautions are ⎸ to eliminate ionization of low-ionization po⎸ impurities, the measurements of ϕ_+ using Eq. ⎸ in the same way as for electron emission app⎸ be reliable. The constant $A_+ = 2\pi k^2 eM/h^3$ ⎸ closely verified. A test for consistency in ⎸ the emission of electrons, atoms, and ions takes ⎸ from one crystalline surface (it is difficult to guar⎸ this), is that

$$\phi_+ + \phi_- = U + V$$

where U is the heat of evaporation of a metal ⎸ and V is the ionization potential of the metal ⎸ all quantities pertaining to the same tempera⎸ The energy balance arises from a cycle in whic⎸ atom is removed from the surface, ionized at a ⎸ tance, and the electron and ion separately are pl⎸ back on the surface. In the case of Mo

$$\phi_+ + \phi_- = 8.6 + 4.2 = 12.8 \text{ ev}$$
$$U + V = 5.75 + 7.15 = 12.9 \text{ ev}$$

balancing within experimental error. Because of ⎸ fact that several crystalline surfaces may be exp⎸ during the measurements it could be that the ex⎸ mentally determined quantities should not q⎸ produce a closed energy cycle. The best ex⎸ mentally determined values of ϕ_+ for Mo and ⎸ appear to be

	ϕ_+
Mo	8.6 ev
W	11.9 ev

It is to be expected that the metallic ions emit⎸ from a hot metal should be emitted with a M⎸ wellian distribution of velocities just as electr⎸ are. This has been verified [11] experimentally ⎸ the case of tungsten.

Other metals which are known to emit positi⎸ ions at temperatures below their melting points a⎸ Cr, Fe, Ni, Cu, Nb, Ru, Rh, and Ta.

2. Polycrystalline Metals

Field Effects Resulting from Polycrystallin⎸ Surfaces. In the section above on the thermioni⎸

work function ϕ it was stated that different exposed crystallographic planes of a crystal possessed somewhat different work functions. Consequently, a surface of polycrystalline metal will in general have a number of different crystallographic surfaces exposed so that the surface as a whole will exhibit areas or patches of different work functions. Thus at best the thermionic-emission current from such a surface would be a composite of emission currents characteristic of each patch. The situation is further complicated by the fact that there does not exist a situation where the electric field is zero over the entire surface. This situation arises from the fact that a local electric field always exists between neighboring patches with different work functions. This is illustrated in Fig. 6.3. The electric field is
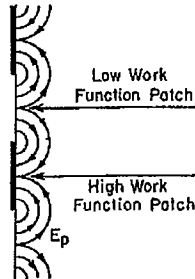
Fig. 6.3. Electric field in the neighborhood of a surface with patches of different work functions.

always directed so as to aid the eléctrons in getting away from the high work-function patch and to hinder the electrons from getting away from a low work-function patch.

The local field between two adjacent patches with work functions ϕ_a and ϕ_b will be the same as that produced by replacing the patches with conductors the difference in whose potentials is $\phi_a - \phi_b$. A surface with repetitive patches of different work functions will produce a local patch field which decreases exponentially with the distance away from the surface and will have reached $1/e$ of its value at the surface in a distance comparable with the mean diameter $\bar{D}$ of the patches. At distances large compared to $\bar{D}$ the potential assumes a value equal to the surface average of the potential of all the patches, i.e.;

$$\bar{\phi} = \sum_i f_i \phi_i \qquad (6.22)$$

where f_i is the fraction of the area whose work function is ϕ_i.

In order to obtain some idea of the type of patch that contributes most of the electrons during thermionic emission, the potential energy of an electron as a function of distance away from the surface at the center of a low work-function patch will be compared to that of an electron leaving the surface at the center of a high work-function patch. Let the work function of the low and high work-function patches be ϕ_l and ϕ_h, respectively.

Referring to Fig. 6.1 and Eq. (6.11), the potential energies in the two cases are

$$W_l = \zeta + \bar{\phi}e - \frac{e^2}{4x} - e \int E_{pnl}\,dx \qquad (6.23a)$$

$$W_h = \zeta + \bar{\phi}e - \frac{e^2}{4x} - e \int E_{pnh}\,dx \qquad (6.23b)$$

where E_{pnl} and E_{pnh} are the normal components of the patch field at the centers of the low and high work-function patches, respectively. If the surface is covered with patches equal in size, then

$$E_{pnl} > 0 \qquad E_{pnh} < 0 \qquad \text{and} \qquad E_{pnh} = -E_{pnl}$$

Since

$$|E_{pnh}| \approx \frac{\phi_h - \phi_l}{\bar{D}} \qquad W_h \geq W_l$$

and for $x \approx \bar{D}$, W_h is likely to be greater than $\zeta + \bar{\phi}e$ for some values of x. The qualitative behavior of W_l and W_h as a function of x is shown in Fig. 6.4.

Thermionic Emission from a Patchy Surface. When there is no applied field present and space-charge fields can be neglected, Fig. 6.4 shows that it is

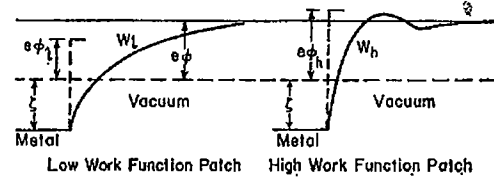Low Work Function Patch   High Work Function Patch

Fig. 6.4. Potential energy of an electron as a function of distance from the emitter surface for low and high work-function patches.

likely that most of the emission current will come from the low work-function patches because of the higher potential barrier in the case of the high work-function case. If, under these circumstances, a weak field E_a is applied so that $|E_a| \ll (\phi_h - \phi_l)/\bar{D}$, then this field will alter the low work-function barrier W_l in the same way as the normal barrier depicted in Fig. 6.1 was altered. Since the thermionically emitted electrons come over this barrier predominantly, the emission current will be given by a modification of Eq. (6.14) or

$$j = f_l A (1 - r_l) T^2 \exp\left(-\frac{\bar{\phi}e - e\sqrt{eE_a}}{kT}\right) \qquad (6.24)$$

where f_l is the fraction of the surface area covered by low work-function patches. Thus for low applied fields the emission current will depend on the field like the normal Schottky effect. This is represented by the low field portion of Fig. 6.5.

An easier situation to treat occurs when the applied field is strong, that is, when $|E_a| \gg (\phi_h - \phi_l)/\bar{D}$. Then one may proceed as though there were no patch fields and the emission from each patch is independent of that of its neighbor. Hence the emission current from the ith patch is

$$j_i = f_i A (1 - r_i) T^2 \exp\left[-\frac{e(\phi_i - \sqrt{eE_a})}{kT}\right] \qquad (6.25)$$

and the total current density is

$$j = AT^2\left[\sum_i f_i(1 - r_i) \exp\left(-\frac{e\phi_i}{kT}\right)\right]$$

$$\exp\left(+\frac{e\sqrt{eE_a}}{kT}\right) \quad (6.26)$$

For this high field case the dependence of j on E_a is again that of the normal Schottky effect and is illustrated by the high field portion of Fig. 6.5. The current is considerably higher through this region because the retarding field at the low work function has been neutralized and thus the low work-function areas are now contributing strongly and the effective surface area is increased over that of the low field region.
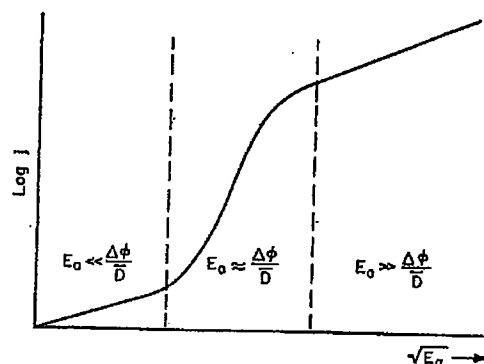
Fig. 6.5. Variation of emission current as a function of applied electric field for a surface with patches of different work functions.

In the intermediate field region where $E_a \approx (\phi_h - \phi_l)/\bar{D}$ the applied field is beginning to neutralize the patch field and by the time the patch field is neutralized the effective work function has been decreased approximately by $\delta\bar{\phi} = \phi - \phi_l$ in addition to the $\sqrt{E}$ effect. In this region the slope of the $\log j$ vs. $\sqrt{E}$ curve is considerably greater than for the other two regions. This is shown in the intermediate region of Fig. 6.5. The behavior in this region is sometimes referred to as the *anomalous Schottky effect*. It is noticeable in the emission from any patchy surface whether made up of clean polycrystalline surfaces or a surface with patches of foreign material. By carefully investigating the dependence of the emission current as a function of the applied field it is possible to obtain information about the size of the patches and the differences in their work functions.

3. Metals with Adsorbed Monolayers

General Facts. It has been realized since the experiments of Langmuir on thoriated tungsten wire that monolayers of adsorbed atoms on pure metal surfaces have a surprisingly large effect on the thermionic emission current at a given temperature. For a complete monolayer the zero-field-emission

TABLE 6.2

Substance, polycrystalline base metal	$A(1 - r)$	ϕ, ev	Ionization potential, ev
Ba	....	2.49	5.19
Cs	....	1.81	3.87
Mg	....	3.60	7.61
Ni	30	4.6	7.61
Th	60.2	3.35	
W	60.2	4.52	8.1
Zr	3×10^3	4.50	6.92
Th on W	3.0	2.63	
Zr on W	5.0	3.15	
O on W	5×10^{11}	9.1	

current obeys Eq. (6.1) but the values of r and ϕ are usually quite different from those for clean metals. Some interesting comparisons are shown in Table 6.2.

When the ionization potential V_i of the adsorbed atoms is of the order of, or not too much greater than, the thermionic work function ϕ_b of the base metal, the effect of a monolayer of these atoms is to decrease the work function ϕ_e of the composite surface. For example, the work function ϕ_e of a surface composed of a monolayer of atoms which will remain adsorbed on tungsten at sufficiently high temperatures whose ionization potential V_i is less than about 7.5 ev will be less than the work function ϕ_W of pure tungsten. Thus $\phi_e < \phi_W$ for monolayers of the alkali metals, the alkaline earths, and such metal atoms as thorium and zirconium on tungsten. On the other hand the work function of tungsten is not appreciably reduced by an adsorbed monolayer of magnesium atoms ($V_i = 7.6$ ev).

Atoms possessing an appreciable electron affinity so that they can exist stably as negative ions can materially increase the work function of a metal when a monolayer is adsorbed on it. For example, a monolayer of oxygen or sulfur on tungsten increases the work function of tungsten by about a factor 2 (Table 6.2).

If θ is the fraction of the surface of the base metal covered by a monolayer of adsorbed atoms of a given kind, then the average work function of a partially coated surface can be found by applying formula (6.22). If ϕ_b is the work function of clean base metal, ϕ_{ad} the work function when the metal has a completed monolayer, the average work function $\bar{\phi}_\theta$ of a partially coated surface is

$$\bar{\phi}_\theta = \theta\phi_{ad} + (1 - \theta)\phi_b . \quad (6.27)$$

or $\qquad \bar{\phi}_\theta = \phi_b + (\phi_{ad} - \phi_b)\theta$

$\bar{\phi}_\theta$ is shown as a function of θ in Fig. 6.6 for two cases; thorium on tungsten and oxygen on tungsten. The curve for thorium on tungsten shows that the work function is a minimum when the tungsten surface is completely covered with a monolayer of thorium. As more layers of thorium are added, the work function gradually increases until the work function of bulk thorium is attained. It is rather typical of some metal layers that the work function for a monolayer of one metal on another is lower than the work function of either metal alone.
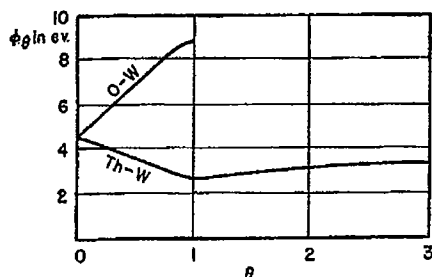
FIG. 6.6. The variation of the average work function of thorium on tungsten and oxygen on tungsten as a function of the fraction of tungsten surface covered.

Explanation of Modified Work Function.
When an atom which has an ionization potential V_i is brought near a metal surface whose work function ϕ is greater than V_i, there is a tendency for the outer electron belonging to the atom to be captured by the metal since this situation represents a lower energy configuration. This leaves the atom ionized and when a monolayer of such ions covers the metal surface a charge double layer results and the field thus produced reduces the work function. This early explanation in this simple form does not quite suffice to explain why it is that some atoms whose ionization potential is somewhat greater than the work function of the base metal will nevertheless give rise to a reduced work function when deposited on a base metal. Such a situation exists when a monolayer of barium, $V_i = 5.19$ ev, is deposited on tungsten, $\phi_W = 4.52$ ev. In such cases the reduction in work function is not as great as for the case when $V_i < \phi_b$. It is very much as though the layer of adsorbed atoms was only partially ionized.

The phenomena described above can be understood with the help of Fig. 6.7a and 6.7b. In these figures the heavy curves denote the potential energy of an electron. At the left of the figure the potential energy of the surface of the metal is depicted together with the energy states in the metal filled with electrons similar to the situation in Fig. 6.1. At the right of Fig. 6.7, the potential energy of an outer electron in an isolated atom with ionization potential V_i is represented. Fig. 6.7a deals with the situation where V_i is a little less than the work function ϕ_b of the base metal. When the free atom is brought in the neighborhood of the metal surface, an interaction takes place and the discrete energy state occupied by the outermost electron in the free atom becomes broadened into a band of states of considerable width. In general the broadening is greater the less the ionization potential. If none of the broadened states lies below the top of the Fermi level in the metal when the atom is on the surface, the atomic electron will leave the atom entirely and reside in the metal leaving the atom ionized, thereby establishing a strong double layer and producing an appreciable decrease in the work function. However, if part of the band of states lies below the Fermi level as actually depicted in Fig. 6.7a these states can be occupied by an electron part of the time by tunneling. Under these circumstances the adsorbed atoms will not be completely ionized
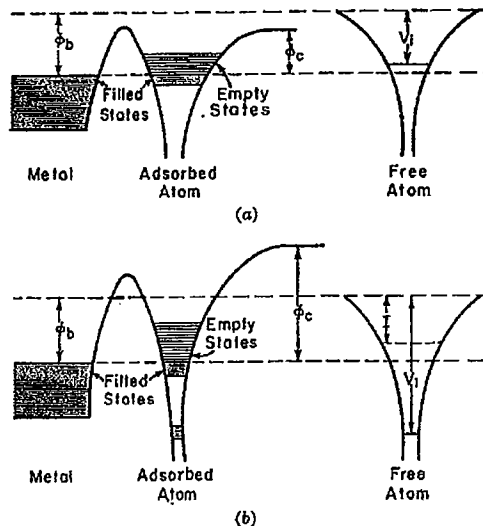

(a)

(b)

FIG. 6.7. Potential energy curves for single atoms and atoms adsorbed on the surface of a metal illustrating the mechanism of lowering or raising the work function.

and the resulting charge double layer will not be as strong and the work function of the monolayer ϕ_c will not be so much smaller than ϕ_b as in the first case. Thus it can readily be seen why the work function can be reduced even though $V_i > \phi_b$ because even here some of the states in the broadened band can lie above the Fermi level in the metal, in which case the layer of atoms will still be partially ionized. From experiments it has been found that when $V_i = 7.6$ ev (magnesium) and $\phi_b = 4.52$ (tungsten) no reduction in work function is found so that no energy states in the broadened band lie above the Fermi level. Figure 6.7b depicts the case where the adsorbed atom has an electron affinity as a free atom. Such atoms are oxygen, chlorine, etc., which can exist stably as negative ions. In oxygen the electron affinity I or work necessary to remove the extra electron is of the order of 3 ev. This situation is depicted at the right of Fig. 6.7b. The energy state occupied by the outermost electron in the neutral atom is shown by the solid line together with the corresponding ionization potential V_i. The dashed line denotes the energy state that can be occupied by an extra electron together with the corresponding electron affinity I. When this atom is brought to the surface, the deep lying energy state occupied by the outermost electron of the normal atom is only broadened a little and lies much lower than the Fermi level in the metal so these states remain filled, there being no exchange of electrons between atom and metal. The upper normally unfilled level represented by the dashed line at the right is greatly broadened and some of its states will almost certainly lie below the Fermi level. Since all these states are empty to begin with, some of them become occupied by electrons from the metal as shown. This again produces a charge double layer but in this case the adsorbed atoms are negative. This requires the electrons from the metal to do more

work in escaping so that the work function ϕ_e is greater than ϕ_b as shown in Fig. 6.7b.

The mechanism described above by which the work function of a base metal is raised or lowered by the adsorption of monolayers of various atoms seems to be adequate to account for the changes in work function found experimentally.

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